



# Zinc glycerolate as a novel heterogeneous catalyst for the synthesis of fatty acid methyl esters



Deborath M. Reinoso, Daniel E. Damiani, Gabriela M. Tonetto\*

Planta Piloto de Ingeniería Química PLAPIQUI (UNS – CONICET), Camino “La Carrindanga” Km 7, CC 717, CP 8000 Bahía Blanca, Argentina

## ARTICLE INFO

### Article history:

Received 21 March 2013

Received in revised form 17 June 2013

Accepted 9 July 2013

Available online 18 July 2013

### Keywords:

Zinc glycerolate

Transesterification

Biodiesel

Soybean oil

Heterogeneous catalyst

## ABSTRACT

In this work, zinc glycerolate (ZnGly) is studied as a new catalyst for an environmentally friendly production of biodiesel. The solid was prepared by a simple procedure, characterized and studied in the transesterification of soybean oil with methanol.

ZnGly was able to convert soybean oil into fatty acid methyl esters with 66–76% yield and up to 95–97% triglyceride (TG) conversion in the 100–140 °C reaction temperature range studied. The catalyst showed a long life and could be reused for five catalytic cycles without deactivation or selectivity loss.

The catalyst exhibited good tolerance toward 0.5 wt.% water, without important changes in the TG conversion, but with a 23% decrease in FAME yield.

In the presence of 10 wt.% fatty acids, ZnGly showed an almost complete TG conversion with an increase in FAME yield of 51% (93% FAME selectivity at 50 min reaction time). At 140 °C and in acid oil, ZnGly can be easily transformed into Zn carboxylate and partially re-generated in the presence of glycerol.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Biodiesel is a liquid biofuel produced from animal fats and vegetable oils, of which rapeseed, sunflower and soybean oils are the most commonly used raw materials.

Biodiesel production can be considered an environmentally friendly activity, by contributing to reduce pollution caused by used oils and fats. Biodiesel is a “clean” fuel because it helps to reduce global CO<sub>2</sub> emissions compared to petroleum-derived diesel, it produces less pollutant gases, its combustion generates less SO<sub>2</sub> emissions, it is biodegradable and non-toxic, and has a high level of lubricity.

Biodiesel is used as a source of energy, for example blended with petrodiesel for the mass market (in Argentina a 7% biodiesel blend is currently used) or in small and medium-size agro-industrial activities.

Industrially, biodiesel is produced by transesterification of triglycerides with an alcohol (usually methanol or ethanol) by homogeneous base catalysis (sodium or potassium hydroxide or alkoxide). Small factories with different feed qualities (using refined and reused oils at the same time) generally use batch processing. Continuous processes, however, are more adequate for

larger factories that can afford larger staffs and require a more uniform feed.

Homogeneous base catalysts present some disadvantages, such as the formation of soap due to the neutralization of free fatty acids (FFA) present in low-quality oils, or the saponification of triglycerides in the presence of water.

The use of a heterogeneous catalyst would simplify the separation and purification steps. There is a growing interest in finding a solid catalyst that is active in the transesterification of triglycerides, while it is selective with raw materials of low quality, that is to say a catalyst that is stable in the presence of FFA and water. Given that it will be used in “green” processes, it should also be non-pollutant and non-toxic.

In previous works [1,2] on soybean oil transesterification catalyzed by zinc carboxylate salts at 140 °C, the formation of zinc glycerolate (ZnGly) was observed in the reaction medium (for zinc laurate, palmitate and stearate). Zn acetate was less stable, and the transformation started at 100 °C. Similar results were found using zinc hydroxide acetate and zinc hydroxide nitrate salts as heterogeneous catalysts. The former solid transformed into ZnGly in the reaction medium at 100 °C, and the latter at 140 °C.

In view of these results, zinc glycerolate was synthesized, and preliminary experiments at 140 °C [1] showed an oil conversion of 80.2% with a FAME yield of 50.9% in the transesterification of soybean oil with methanol. No reports on the use of Zn monoglycerolate as catalyst in the synthesis of biodiesel were found in the literature. The most similar reference is the use of calcium diglyceroxide as the active phase in the transesterification of triglycerides

\* Corresponding author. Tel.: +54 291 4861700; fax: +54 291 4861600.

E-mail addresses: [gtonetto@plapiqui.edu.ar](mailto:gtonetto@plapiqui.edu.ar), [gtonetto@yahoo.com.ar](mailto:gtonetto@yahoo.com.ar) (G.M. Tonetto).

[4–7]. This solid has a similar structure, the same anion, and they are also similar in the sense that both can be formed in the reaction medium if the cation is present.

Zinc glycerolate is classified as non-irritant, and it is widely used in pharmaceutical formulations with therapeutic or prophylactic properties, in cosmetic industries, veterinary product and as a lubricant and as a polymer stabilizer [8–10]. The synthesis of ZnGly is an economical and simple procedure [11]. ZnGly has potential as a new clean catalyst for an environmentally-friendly biodiesel production.

The goal of the present work was to investigate ZnGly as a novel and green catalyst in the transesterification of soybean oil with methanol. Its stability in consecutive reuses, and the effect of water and fatty acid were studied.

## 2. Experimental

### 2.1. Catalyst preparation

The zinc glycerolate solid was synthesized according to the procedure reported by Dong and Feldman [11] with slight modifications. The salt preparation was carried out in a Parr reactor under N<sub>2</sub> atmosphere (30 psi). An amount of 0.05 mol zinc acetate dihydrate (99% Sigma–Aldrich) and 3.4 mol of glycerol with 2% of water was fed into the reactor and heated up to 160 °C for 1 h at 500 rpm. The resulting precipitate was filtered, washed with ethanol and dried for 1 h at 40 °C.

### 2.2. Catalyst characterization

The catalyst structure (synthesized and recovered after reaction) was validated by X-ray diffraction (Philips PW1710, using Cu K $\alpha$  radiation scan in the 2 $\theta$  range 2°–60°) and by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS, Nicolet 6700FT-IR spectrometer).

The morphological properties of the solids were obtained from the N<sub>2</sub> adsorption isotherm at 77 K by the BET method using a Nova 1200e Quantachrome instrument, and the pore size distribution was calculated by the BJH method. The catalyst particle size distribution was evaluated using a Partica LA-950 V2 Laser Diffraction Particle Size Distribution Analyzer (HORIBA), and the morphology of the powder catalysts was analyzed by SEM (JEOL 35 CF scanning electron microscope).

The thermal stability of the catalysts was determined using a thermogravimetric analyzer (Discovery TGA) under N<sub>2</sub> flow from room temperature to 800 °C (at a heating rate of 20 °C/min).

The amount of Zn in the catalysts (before and after reaction) was determined by atomic adsorption spectrometry (AAS, Perkin Elmer Analyst 700).

The acidity of the solid was analyzed by potentiometric titration. The catalyst was dispersed in acetonitrile and titrated with a 0.1 N *n*-butylamine solution dissolved in the same solvent [12].

The basicity of the solid was estimated by the benzoic acid titration method using indicators. A slurry with 100 mg of ZnGly and the indicators (bromothymol blue and phenolphthalein) was titrated with a 0.01 M solution of benzoic acid in methanol [13].

### 2.3. Catalytic tests

The catalytic tests were carried out in a 600 cm<sup>3</sup> Parr reactor (internal diameter: 64 mm) operated in batch mode, equipped with a 4-angled blade stirrer.

The reaction was studied at 100 and 140 °C, with an agitation rate of 500 rpm, and a reaction time of 2, 4 and 6 h. The raw materials and the catalyst were fed into the reactor and then the system was heated up until reaction temperature was reached. At that moment, the agitation was started and a zero time sample was taken.

For the reaction, soybean oil (Argentinian commercial brand) without any special pretreatment and methanol (UVE HPLC) were used. The methanol/oil molar ratio was 30:1, and the catalyst loading was 3 wt.% (with respect to oil).

Additional experiments were conducted in order to quantify the influence of external mass transfer: the catalytic tests were performed at different agitation rates (from 300 to 1000 rpm). In order to study the reusability of the samples, five consecutive tests were performed at 140 °C (the solids were washed with hexane and ethyl ether/ethyl alcohol solution (50/50)). The effect of water and free fatty acid content on the transesterification reaction was investigated (in separate experiments) by adding 0.5 wt.% of water (with respect to oil) or 10 wt.% of saturated fatty acid [14] (stearic acid, Sigma–Aldrich  $\leq 99\%$ , with respect to oil) into the reaction medium under the conditions described above.

Reaction samples were centrifuged to improve the separation of methanol from the oil phase. A ~50 mg sample was taken from the oil phase and prepared for chromatographic analysis. The chromatography of the reactants and products was carried out in a Perkin Elmer AutoSystem XL equipment with a DB-17HT capillary column and a FID detector (according to the standard UNE-EN 14105 norm).

In addition, fatty acid content of each reaction sample (polar and non-polar phases) was determined by titration according to norm UNE-EN 14104.

The triglyceride (TG) conversion (*X*) and FAME yield (*Y*) were calculated using the following equations:

$$X_{TG} = \frac{\text{mol TG}_{t_0} - \text{mol TG}_{t_f}}{\text{mol TG}_{t_0}} \quad (1)$$

$$Y_{FAME} = \frac{\text{mol FAME}_{t_f}/3}{\text{mol TGE}_{t_0}} \quad (2)$$

where TGE is the triglyceride molar equivalent,

$$\text{mol TGE} = \text{mol TG}_{t_0} + \frac{2}{3} \text{mol DG}_{t_0} + \frac{1}{3} \text{mol MG}_{t_0} + \frac{1}{3} \text{mol FFA}_{t_0} \quad (3)$$

Five independent transesterification reactions were carried out (under the above specified operating conditions) to review the variability and repeatability of the results and determine the overall experimental error (of the catalytic test and chromatographic determination). The overall standard error calculated was  $\pm 0.7\%$  for TG conversion and  $\pm 1.6\%$  for FAME yield.

For the esterification reaction, oleic acid (OA, Anedra 61.5%) was used. The molar ratio of alcohol to OA was 30:1, and the catalyst loading was 3 wt.% (with respect to OA). OA concentration was measured according to norm UNE-EN 14104.

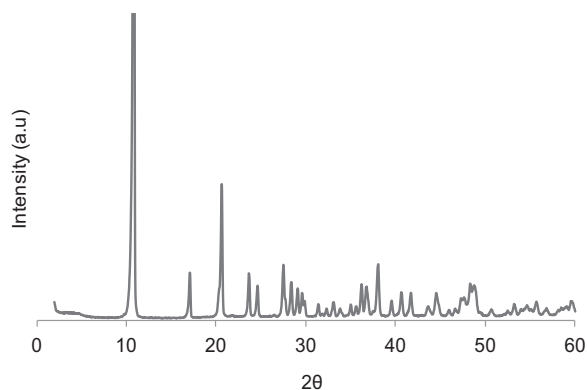
## 3. Results and discussion

### 3.1. Characterization of the synthesized Zn glycerolate

The morphological properties of synthesized Zn glycerolate are shown in Table 1. The solid presented a low surface area, 1.3 m<sup>2</sup>/g, with a pore radius of 21.7 nm.

**Table 1**  
Morphological properties of the zinc glycerolate.

Properties	ZnGly
Specific surface area (m <sup>2</sup> /g)	1.3
Pore volume (cm <sup>3</sup> /g)	0.01
Pore radius (Å)	21.7
Particle size (μm)	26.6



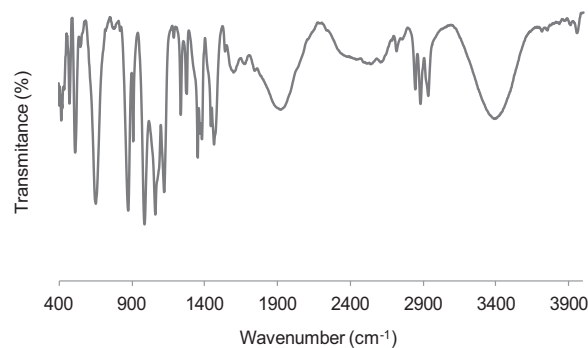
**Fig. 1.** X-ray diffraction pattern of the synthesized Zn glycerolate. Reference: peak used for basal spacing and crystal size.

The X-ray diffraction pattern of synthesized catalyst is shown in Fig. 1. The XRD pattern for the solid presented characteristic peaks located at  $2\theta = 10.9^\circ$  (1 0 0),  $20.67^\circ$  (1 1 1),  $17.12^\circ$  (0 0 1), and  $27.53^\circ$  (2 1 1) which according to the JCPDS card No. 00-23-1975, are assigned to the crystal phase of Zn monoglycerolate ( $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$ ). The basal spacing ( $d_{h00}$ ) was 8.02 Å calculated according to Bragg's law, and the apparent size of the crystal was 7.96 Å determined by the Scherrer method.

Some differences in the relative intensity values between this diffractogram and the JCPDS card are observed, especially in the case of the signal at  $10.9^\circ$ , which could indicate the development of some preferred axis. Das and Khushalani [15] reported the synthesis of zinc glycerolate crystals with crystallographic preferred orientation along the (1 0 0) axis. Hambley and Snow [16] indicated that the zinc atoms bridge the glycerolate molecules forming polymeric sheets lying parallel to each other, and the aliphatic hydrogens are arranged in the space between the layers. Therefore it can be assumed that the preferential orientation observed in the (1 0 0) plane is due to the layered-like structure of ZnGly [15].

The FTIR spectrum of the zinc salt is shown in Fig. 2. The characteristic signals of the alcoholic C–O stretching mode are present at  $1054$  and  $1124\text{ cm}^{-1}$ . The peaks at  $1468$  and  $1675\text{ cm}^{-1}$  were attributed to the O–H bending mode. The regions at  $3000$ – $3500\text{ cm}^{-1}$  correspond to physically adsorbed water, glycerol O–H stretching mode and hydrogen bonding. The band at  $1943\text{ cm}^{-1}$  assigned to C–O stretching mode, where the oxygen atom is involved in hydrogen bond, confirms the formation of a zinc glycerolate phase. The presence of the Zn–O bond in the sample was confirmed with the peak at  $550\text{ cm}^{-1}$  [15].

The SEM micrograph of the solid catalyst is presented in Fig. 3. It reveals that Zn glycerolate consists of platelets with small granules



**Fig. 2.** DRIFT spectrum of the synthesized Zn glycerolate.

on the surface. The irregular plates have different particle sizes and a thickness of about 950–960 nm.

The curves for thermal gravimetric and the differential thermogravimetric analysis of Zn glycerolate are shown in Fig. 4. The thermal decomposition process occurred in the temperature range  $380$ – $450^\circ\text{C}$  through the oxidation of the organic matrix, forming the metal oxide. The observed total mass loss in the solid decomposition was close to 46%. This value confirms the synthesis of zinc monoglycerolate.

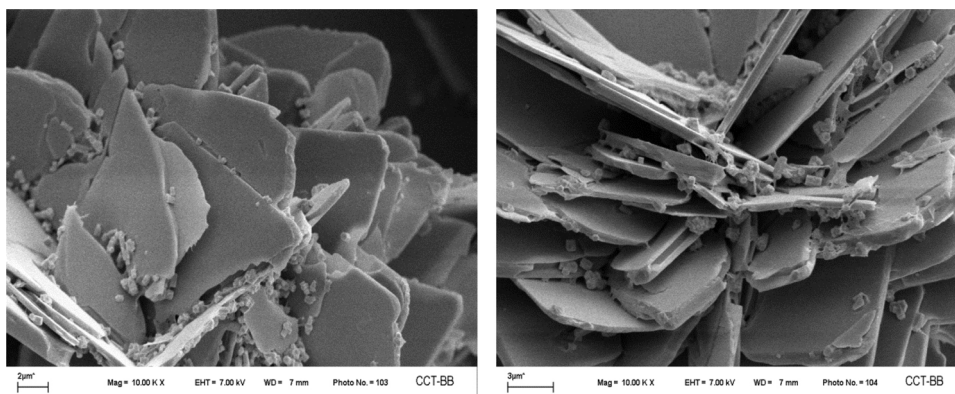
The acidity of de solid was analyzed by potentiometric titration. The maximum acid strength (MAS) is indicated by the initial electrode potential  $E$  (mV). For the studied solid, MAS had a value of approximately  $-97.7\text{ mV}$ , which corresponds to very weak sites according to the following scale proposed by Cid and Pecchi [12]:  $E > 100\text{ mV}$  for very strong sites,  $0 < E < 100\text{ mV}$  for strong sites,  $-100 < E < 0\text{ mV}$  for weak sites, and  $E < -100\text{ mV}$  for very weak sites.

The basicity of ZnGly was estimated by benzoic acid titration of the base sites in the presence of a pH indicator. This technique provides a first indication of the total basicity of the solid [17]. The number of weak base sites (as measured in the titration with bromothymol blue) was  $8 \times 10^{-2}\text{ mmol/g cat.}$  The number of the stronger base sites can be measured with phenolphthalein as indicator. In the case of ZnGly, the presence of stronger base sites was not detected.

### 3.2. Catalytic activity

#### 3.2.1. Mass transfer resistance in the transesterification of soybean oil with methanol

Catalyzed heterogeneous transesterification is a reaction with two immiscible liquid phases and a solid catalyst, making it very



**Fig. 3.** SEM image of synthesized Zn glycerolate.

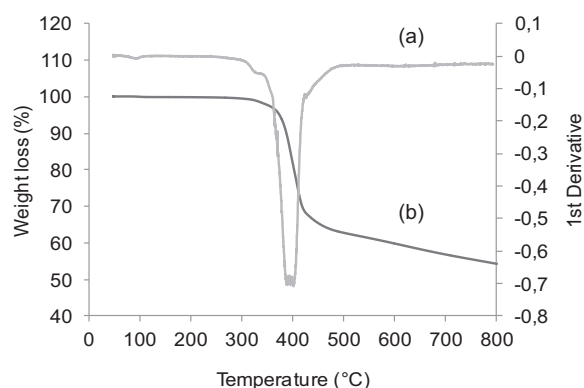


Fig. 4. TGA (a) and DTG (b) curves for Zn glycerolate.

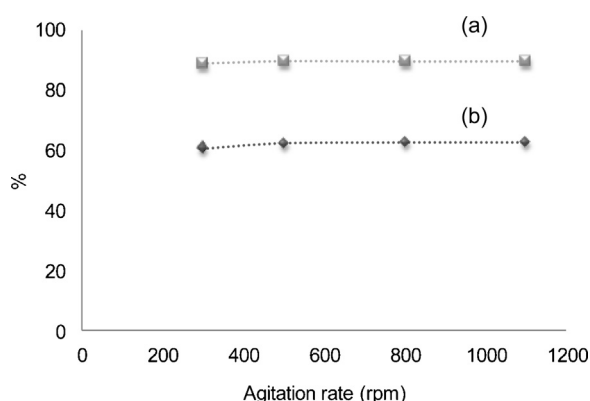


Fig. 5. Triglyceride conversion (a) and FAME yield (b) at different agitation rates for Zn glycerolate catalyst at 140 °C.

important to determine if the reaction is under kinetic or diffusion control.

In order to quantify the impact of external mass transfer resistance on the reaction rate, the transesterification reaction was studied at different agitation rates from 300 to 1100 rpm. The experiments (presented in Fig. 5) showed that the triglyceride conversion and FAME yield were independent of the agitation rate above 300 rpm. Hence, all further experiments were conducted at an agitation rate of 500 rpm to ensure that there was no external mass transfer resistance.

The Weisz–Prater criterion (Eq. (4)) was used to evaluate the intraparticle diffusion limitations for triglyceride (TG):

$$\Phi_{TG} = \frac{(-r_{obs,TG})\rho_c D_p^2}{36D_{eff,TG} C_{TG}} \quad (4)$$

where  $r_{obs,TG}$  is the initial observed TG reaction rate at 140 °C [ $4.02 \times 10^{-5}$  mol/s kg<sub>cat</sub>],  $\rho_c$  is the apparent density of the catalyst [kg/m<sup>3</sup>],  $D_p$  is the particle diameter [ $2.67 \times 10^{-5}$  m],  $D_{eff}$  is the effective diffusion coefficient [m<sup>2</sup>/s], and  $C_{TG}$  is the TG concentration [467 mol/m<sup>3</sup>]. The effective diffusivity is given by:

$$D_{eff,i} = \frac{D_i \cdot \varepsilon}{\xi} \quad (5)$$

The Weisz–Prater criterion indicates that the mass transfer limitation for the unknown kinetics is negligible when  $\Phi_i < 0.03$ –0.7 [18].

The tortuosity factor ( $\xi$ ) was selected to be 4 [19], and the porosity ( $\varepsilon$ ) was calculated by:

$$\varepsilon = \rho_c \times V_{pore} \quad (6)$$

Table 2

Transesterification of soybean oil with methanol at 100 and 140 °C (reaction time: 6 h): triglyceride conversion and FAME yield.

Temperature (°C)	360 min	
	TG conversion (%)	FAME yield (%)
100	95.0	65.9
140	96.8	76.6

The triglyceride–methanol diffusion coefficient was evaluated using the Wilke and Chang correlation [20,21]. As methanol is used in large excess, the diffusivity of TG in methanol was considered and calculated by the following expression:

$$D_{TG,MeOH} = 7.4 \times 10^{-8} \frac{\sqrt{\Phi_{MeOH} M_{MeOH}}}{\eta_{MeOH} \nu_{TG}^{0.6}} T \quad (7)$$

where  $D_{TG,MeOH}$ : diffusion coefficient of TG in methanol (cm<sup>2</sup>/s);  $\Phi_{MeOH}$ : association factor of methanol (1.9);  $M_{MeOH}$ : molecular weight of methanol (32 g/mol);  $T$ : temperature (413 K);  $\eta_{MeOH}$ : viscosity of methanol (0.218 cP);  $\nu_{TG}$ : molar volume of TG at 140 °C (1054 cm<sup>3</sup>/mol).

The molecular diffusivity of TG in methanol was  $D_{TG} = 1.52 \times 10^{-9}$  m<sup>2</sup>/s.

In the present experiments, the numerical value of the Weisz–Prater module was  $3 \times 10^{-4}$  for TG, indicating that it is possible to neglect the concentration gradients within the catalyst particle.

The Weisz–Prater module was calculated for TG because it is the reactant of the largest size and it is present in minor concentration.

### 3.2.2. Transesterification of soybean oil with methanol

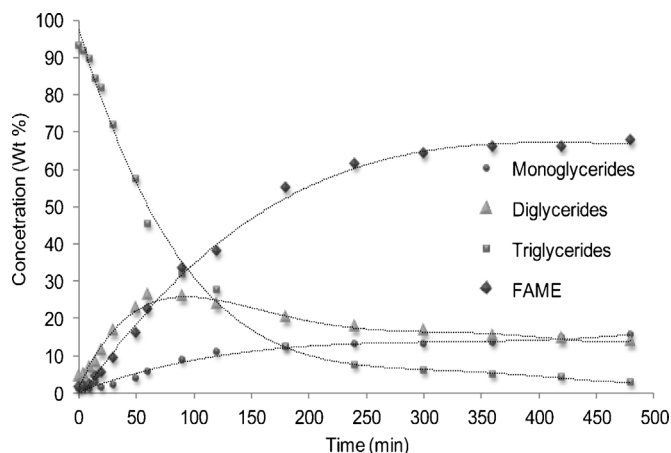
The values of TG conversion and FAME yield at 100 and 140 °C are presented in Table 2, where it can be observed that ZnGly showed good catalytic activity at both working temperatures. At 100 °C and 6 h of reaction, TG conversion was of 95% with a FAME yield of 65.9%. When the reaction temperature was 140 °C, TG conversion reached 96.8% (approximately 2% higher than that observed at 100 °C) with a FAME yield of 76.6% (14% higher than at 100 °C). The increase in yield at the higher temperature is attributed to the fact that the transformation of diglycerides into monoglycerides is the stage that requires more energy [22].

Previously, the presence of weak base sites on the surface of ZnGly was checked. The catalytic activity of the solid is related to these sites. It was proposed in the literature [7,23,24] that when the reaction is catalyzed by a solid base catalyst, the mechanism involves the adsorption and activation of the methanol (by the base sites) as a nucleophilic reactant to attack the electrophilic carbon of carboxylate esters in the triglyceride. This leads to formation of the alkoxycarbonyl intermediate. Then, the intermediate splits into FAME and the anion of diglyceride. In the case of ZnGly, the surface between the polymeric sheets is hydrophobic, therefore the glyceride molecules (TG, DG and MG) can approach easily the chemisorbed methoxide ions [7].

The level of activity presented by ZnGly was good compared to that of other solids of similar basicity. ZnO has weak base strength [25], and it originates a color change for bromothymol blue, but not for phenolphthalein [26]. This solid was not active for the transesterification of vegetable oils at 65 °C [25], but it was effective at 120 °C with 80% FAME yield after 24 h with 12.5 wt.% catalyst [27]. It was also reported a 77.5% FAME yield at 200 °C after 4 h of reaction in the transesterification of crude coconut oil [28].

ZnGly can be also compared with ZrO<sub>2</sub>. This oxide has weak acid and base sites on the surface [29,30]. ZrO<sub>2</sub> presented a 31% TG conversion with an 8.4% FAME yield in the transesterification of





**Fig. 6.** Evolution of products and reactants over time for the Zn glycerolate catalyst at 100 °C.

sunflower oil at 200 °C [29], and 49.3% FAME yield at 200 °C after 4 h of reaction for crude coconut oil [28].

The evolution of the products and reactants over time in the transesterification of soybean oil at 100 and 140 °C (until reaching a constant FAME concentration) is shown in Figs. 6 and 7. In both cases the typical behavior of a reaction in series can be observed, where the concentration of TG decreases to form DG. At 100 °C, the concentration of DG reaches a maximum after 60 min of reaction, whereas at 140 °C this value is reached at 30 min.

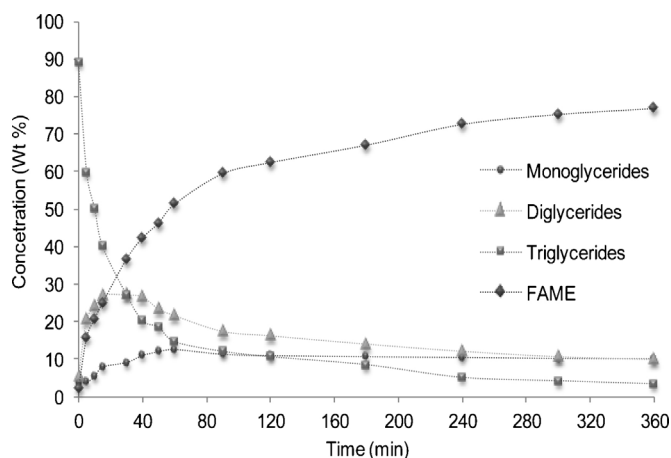
Then the MG are formed, which react to form FAME. At 100 °C the synthesis of MG presents a light increasing trend (Fig. 6), whereas at 140 °C maximum concentration of MG is reached at 60 min (Fig. 7).

FAME concentration reaches a final value of 66.2% and 77% at 100 and 140 °C, respectively. These final concentrations correspond to yields of 65.9 and 76.6% (after 6 h of reaction).

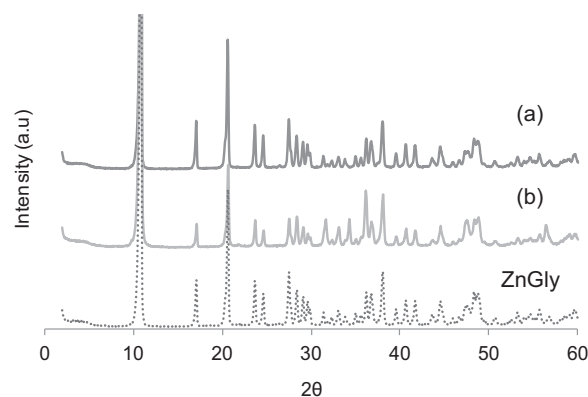
The catalyst used in reaction was recovered by filtration, washed in an ethyl ether/ethyl alcohol solution (50/50) and characterized. The XRD patterns and FTIR spectra for the salt used in transesterification at 100 and 140 °C are shown in Figs. 8 and 9. The diffraction patterns of the solid did not show changes in the crystal structure. For both temperatures, basal spacing was 8.12 Å.

The stability of the catalyst was also confirmed by FTIR. The spectra show the characteristic bands of the zinc salt at 450, 1050, 1124, 1458 and 1943 cm<sup>-1</sup> (mentioned in previous sections).

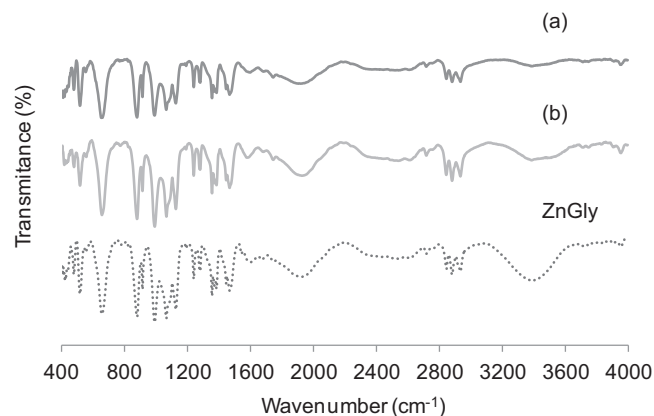
ZnGly was stable in the presence of methanol at both temperatures. This solid is known as a hydrophobic material, lacking



**Fig. 7.** Evolution of products and reactants over time for the Zn glycerolate catalyst at 140 °C.



**Fig. 8.** X-ray diffraction pattern of Zn glycerolate after reaction at 100 °C (a) and 140 °C (b).



**Fig. 9.** DRIFT spectrum of Zn glycerolate after reaction at 100 °C (a) and 140 °C (b).

any strong interactions between the layers. The disposition of the aliphatic hydrogen atoms toward the outside of the layers serves to protect the more polar groups from polar solvents, and so produces the hydrophobic properties [16].

### 3.2.3. Study of the catalysts in consecutive uses in the transesterification of soybean oil

Zinc glycerolate was used in five consecutive runs at 140 °C. The product distribution in each catalytic cycle is presented in Table 3. The results obtained did not show significant changes in activity and selectivity among the experiments.

The zinc content in the catalyst and in the two phases of the reaction mixture was analyzed by atomic absorption spectroscopy. In the case of the synthesized solid, zinc concentration was of 41%, and it remained constant after five catalytic cycles. After 2 h of reaction, the metal was not detected in the polar and non-polar phases.

**Table 3**

Reusability of the catalysts in the transesterification of soybean oil with methanol at 140 °C (reaction time: 2 h): triglyceride conversion and FAME yield.

Composition of the non-polar phase (wt.%)	Catalytic test				
	1	2	3	4	5
Monoglycerides	10.9	14.3	10.9	12.0	11.1
Diglycerides	16.2	13.2	11.9	12.3	17.5
Triglycerides	10.5	6.8	8.9	7.6	6.5
FAME	62.5	65.8	68.8	68.1	65.0
TG conversion (%)	89.5	93.2	91.5	92.4	93.5
FAME yield (%)	62.2	65.5	68.4	67.7	64.6

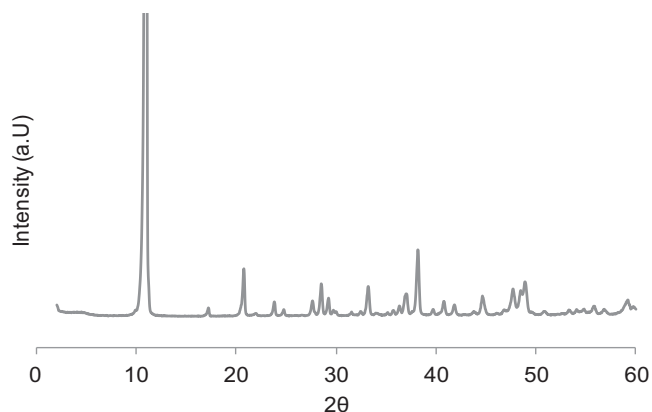


Fig. 10. XRD pattern of used ZnGly catalyst after five reaction cycles in the transesterification of soybean oil at 140 °C.

The XRD pattern of Zn glycerolate after four reuses is presented in Fig. 10. The diffractogram of the used solid indicates that its crystal structure remained constant, and the basal spacing shows no changes after five catalytic cycles (8.12 Å).

ZnGly crystals intensified the peak of (100) plane after being used as catalyst in five reaction cycles of transesterification of soybean oil with methanol at 140 °C (methanol pressure = 160 psi). However, this modification was not observed after the reaction at 100 °C (methanol pressure = 52 psi) (not shown). Considering that the original sample was synthesized at 160 °C in glycerol medium (N<sub>2</sub> pressure = 30 psi), the change in ZnGly crystals could be attributed to the combined effect of pressure, temperature and a non-polar medium (as it is presented in the transesterification reaction medium).

It is reported that temperature, pressure, overall molar ratio of glycerol to zinc, and agitation rate are driving factors in controlling the size of the ZnGly particles [31].

### 3.2.4. Kinetic study

The global reaction for the transesterification of triglycerides in the presence of excess methanol has been reported [32,33] to follow pseudo-first order kinetics:

$$\frac{dX_{TG}}{dt} = k(1 - X_{TG}) \quad (8)$$

where  $X_{TG}$  is the triglyceride conversion, and  $t$  is the reaction time.

Integrating Eq. (8) the overall rate equation ( $k$ ) can be given as Eq. (9),

$$\ln(1 - X_{TG}) = kt \quad (9)$$

Fig. 11 shows the kinetics of the transesterification of soybean oil catalyzed by ZnGly at 100 and 140 °C (Figs. 6 and 7). The graph presents a linear correlation for Eq. (9) indicating that the experimental results followed a pseudo first-order-kinetic model.

The apparent activation energy ( $E_a$ ) for the reaction was determined from the Arrhenius equation (in the reaction temperature range 60–140 °C). Fig. 12 shows the Arrhenius plot, from which an apparent activation energy of 39.2 kJ/mol was obtained. The experimental results presented in Section 3.2.1 showed that the catalytic tests were under no transport limitations. Therefore, the activation energy obtained in the present study corresponds to a reaction truly governed by kinetics.

The calculated activation energy is within the reported range (33–84 kJ/mol) for a wide number of different catalysts [34–37]. For the K-CaO-catalyzed heterogeneous transesterification of wasted cotton oil, the  $E_a$  was 54 kJ/mol [35]. In the case of a base catalyst such as kaolin (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>), the apparent activation energy was 48.9 kJ/mol for the transesterification of soybean oil

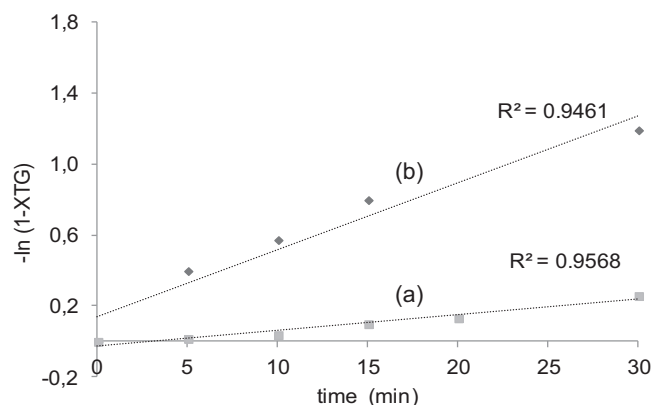


Fig. 11. Plot of  $\ln(1 - X_{TG})$  as a function of reaction time  $t$  at different temperatures. Reference: (a) 100 °C and (b) 140 °C.

in excess methanol [36]. Li et al. [37] found an activation energy of 60.5 kJ/mol for the transesterification of canola oil with ethanol using mixed oxide (Mg<sub>2</sub>CoAl) catalyst.

### 3.2.5. Effects of water on the transesterification of soybean oil

In order to study the effect of the water content on the catalytic activity of the solid, a transesterification test was carried out using 0.5% water (in relation to oil) at 140 °C and under the same conditions used above.

The presence of water in the medium caused a decrease in the activity of the catalyst, with no evidence of hydrolysis, since no free fatty acids were detected in the reaction medium (in neither of the two phases). At 2 h of reaction, a TG conversion of 84.1% and a FAME yield of 48.1% were obtained (Table 4).

The evolution of products and reactants in the transesterification of soybean oil in the presence of 0.5% water is presented in Fig. 13. The concentration of TG fell slowly to a value of 15.9%, whereas the concentration of DG grew to a maximum value of 30% at 60 min, and the MG fraction increased over all the time range analyzed (11.5% at 120 min).

Even though the reaction was slower than in the absence of water (Fig. 7), at the same TG conversion the product distribution was similar for both catalytic tests. For example, for a TG conversion of ~84%, the concentrations of the products in the reaction without water ( $t_{RX} = 60$  min) were DG = 21.6%, MG = 12.5%, FAME = 51.3%. In the presence of water ( $t_{RX} = 120$  min) the concentrations were: DG = 24.3%, MG = 11.5%, FAME = 48.3%.

The XRD pattern and FTIR spectrum of the catalyst used in transesterification at 140 °C are presented in Figs. 14 and 15. The XRD

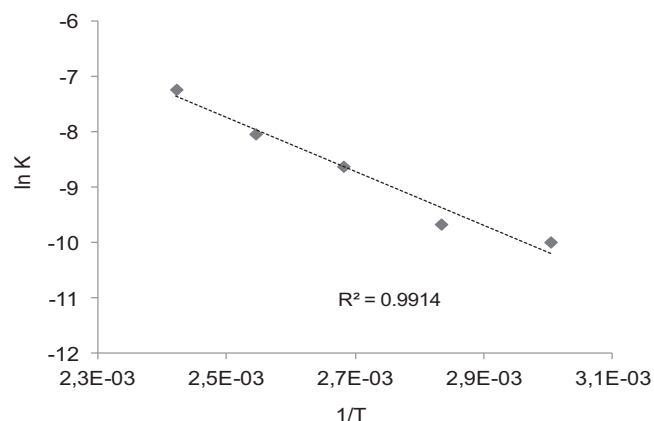
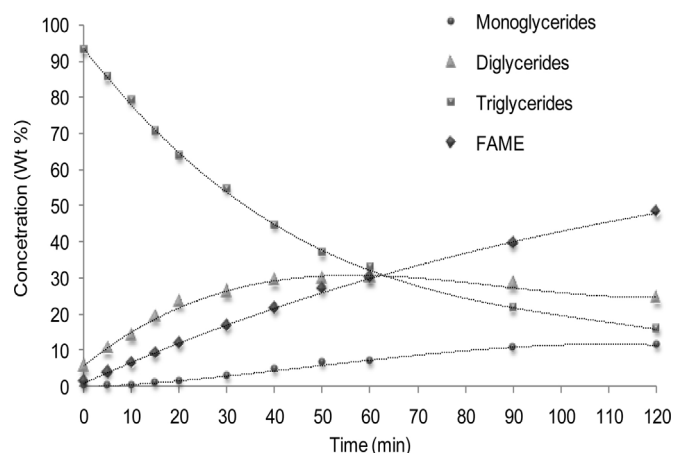
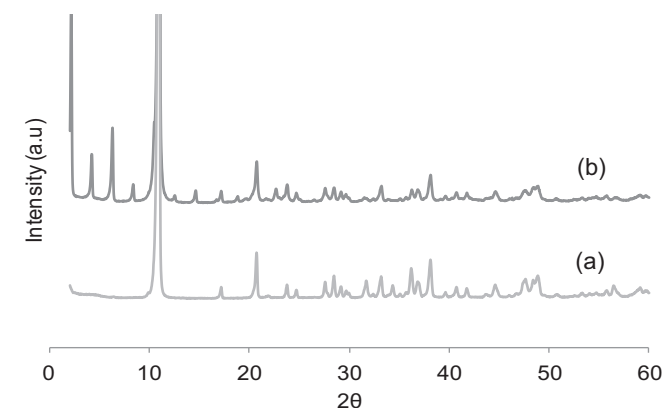


Fig. 12. Plot of  $\ln k$  vs.  $1/T$  for the transesterification of soybean oil with methanol.



**Fig. 13.** Evolution of products and reactants in the transesterification of soybean oil with methanol/0.5% water at 140 °C.



**Fig. 14.** XRD pattern of (a) ZnGly after the transesterification of soybean oil with methanol/0.5% water and (b) ZnGly after the transesterification of soybean oil/10% stearic acid with methanol.

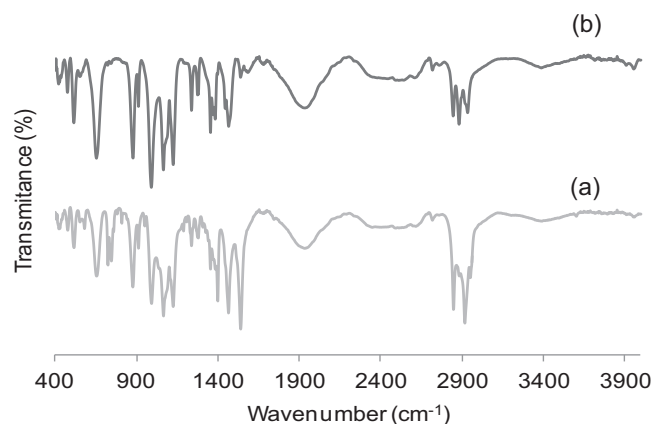
analysis (Fig. 16a) indicates that the crystal structure of the solid did not change, maintaining a basal spacing of 8.10 Å. Confirming this result, the characteristic bands of ZnGly (450, 1050, 1124, 1458, and 1943  $\text{cm}^{-1}$ ) were determined by FTIR (Fig. 17a).

In order to check whether the decrease in catalytic activity in the presence of water was irreversible, the solid was tested in a new experiment with refined oil under the same operating conditions (without added water). At 140 °C, a TG conversion of 90.6% was observed, with a FAME yield of 61.3%. These values are similar to those presented in Table 4 for the new catalyst with refined oil,

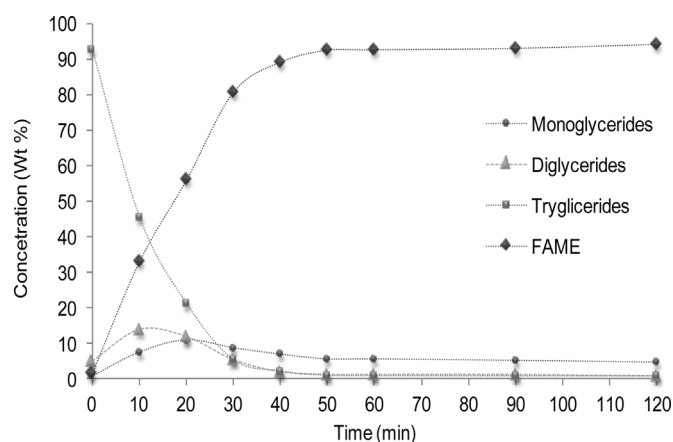
**Table 4**

Transesterification of soybean oil with methanol using ZnGly as catalyst (reaction time: 2 h, temperature: 100 °C): food-grade oil (A), acid oil (B), water-content oil (C).

Composition of the non-polar phase (wt.%)	Soybean oil		
	A	B	C
Monoglycerides	10.9	4.6	11.5
Diglycerides	16.17	0.8	24.3
Triglycerides	10.48	0.5	15.9
FAME	62.41	94.2	48.3
Fatty acids	–	–	–
TG conversion (%)	89.52	99.5	84.1
FAME yield (%)	62.18	93.8	48.1
Initial content (wt.%)			
Water	0	0	0.5
FFA	$1.8 \times 10^{-3}$	10.0	$1.8 \times 10^{-3}$



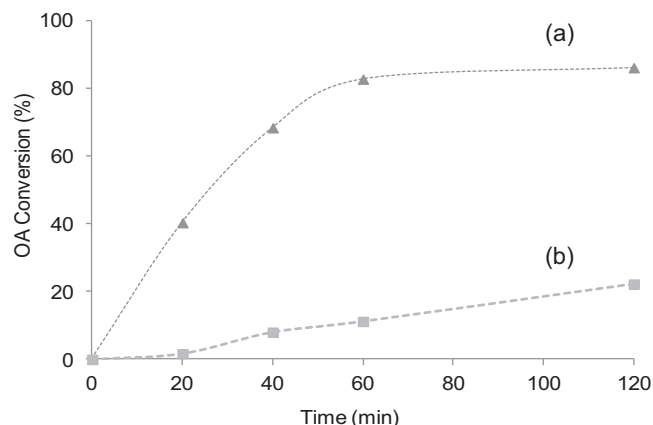
**Fig. 15.** DRIFT spectrum of (a) ZnGly after the transesterification of soybean oil with methanol/0.5% water and (b) ZnGly after the transesterification of soybean oil/10% stearic acid with methanol.



**Fig. 16.** Evolution of products and reactants in the transesterification of soybean oil/10% stearic acid with methanol at 140 °C.

indicating that the decrease in activity with the water addition is reversible.

In order to study the effect of water on ZnGly, the catalyst was mixed in an excess of water at 100 °C for 1 h. The solid was decomposed into glycerol and zinc oxide (determined by IR and XRD, not shown here). Also, the catalyst was mixed in a mixture of 50:50 glycerol:water, at the same temperature and time. In this case, after the experiment, ZnGly was perfectly recovered. This result could



**Fig. 17.** Esterification of oleic acid catalyzed by ZnGly at 100 °C (a) and 140 °C (b).

indicate that the solid can regenerate in the presence of alcohol. This may have occurred in the reaction medium: at the initial time, a fraction of the catalyst surface may have transformed into ZnO, but with the reaction progress, the produced glycerol regenerated the catalyst.

### 3.2.6. Effects of free fatty acids on the transesterification of soybean oil

The effect of the FFA on the performance of the studied reaction was analyzed. The catalytic test was carried out using a high concentration of free fatty acid (10% stearic acid with respect to oil) at 140 °C and under the same conditions used above.

The presence of stearic acid enhanced the performance of the catalyst, reaching a TG conversion of 99.5% and a FAME yield of 93.8% at 2 h of reaction (Table 4). The evolution of the products and reactants during the transesterification with 10% stearic acid is shown in Fig. 16. It can be observed that in this case the equilibrium conversion was reached at 50 min of reaction (99.1%). It is important to point out that no presence of FFA was observed at any time of the reaction (in neither of the phases). The stearic acid was not detected in the initial sample, indicating that the acid reacted during the reactor heating stage (carried out without agitation to prevent the progress of the reaction). In turn, the initial concentration of FAME was lower than 1.7 wt.%, indicating that the decrease in FFA rate is not due to its esterification with methanol.

The characterization of the catalyst recovered after the reaction with 10% stearic acid shows that the material underwent a transformation. The XDR pattern (Fig. 14b) indicates that the sample corresponded to a mixture of zinc stearate ( $2\theta = 2.1^\circ$ ,  $4.2^\circ$  and  $6.2^\circ$ ) [1] and zinc glycerolate ( $2\theta = 10.9^\circ$ ,  $17.4^\circ$  and  $20.7^\circ$ ). The peak located at  $2\theta = 10.9^\circ$  widens by overlapping with the peak corresponding to zinc stearate ( $2\theta = 10.5^\circ$ ), which is formed in the reaction medium.

This transformation is also evident in the FTIR spectrum (Fig. 15b), where typical signals of the carboxylate group can be observed ( $1398$ ,  $1456$ ,  $1535\text{ cm}^{-1}$ ) [1], as well as the bands attributed to zinc glycerolate ( $1050$ ,  $1124$ ,  $1943\text{ cm}^{-1}$ ).

These results show that the stearic acid transformed into zinc stearate during the heating period. The initial amount of catalyst and fatty acid are such that they enable the complete transformation of the stearic acid into zinc stearate.

In turn, as shown in previous works [1], at 140 °C and in the presence of glycerol, carboxylate salts partially transform into Zn glycerolate. This partial transformation originates the mixture of solids observed by XRD in Fig. 14b.

Zn stearate is responsible for the high reaction rate. TG conversion and FAME yield values are comparable to those obtained previously for several carboxylate salts [1].

In order to test the behavior of ZnGly with fatty acids, the solid was used as catalyst in the esterification of oleic acid with methanol at 100 and 140 °C. The results are presented in Fig. 17. At the higher temperature, a conversion of 80% was obtained at 1 h of reaction. At 100 °C, the conversion of the acid was low, reaching 20% at 2 h of reaction. When the used catalyst was analyzed by XRD (Fig. 18) and IR (Fig. 19), it was observed that ZnGly reacted with the carboxylic acid forming the corresponding carboxylate salt at both temperatures.

The transformation cycle of the catalyst presented in this work is outlined in Scheme 1. For the transesterification of an acid oil, initially Zn glycerolate reacts with the carboxylic acids forming Zn carboxylate. During the reaction and in the presence of glycerol, Zn carboxylate transforms again into Zn glycerolate (depending on temperature and time).

In the transesterification of a refined oil, ZnGly remains stable. On the other hand, in the esterification of carboxylic acids, Zn

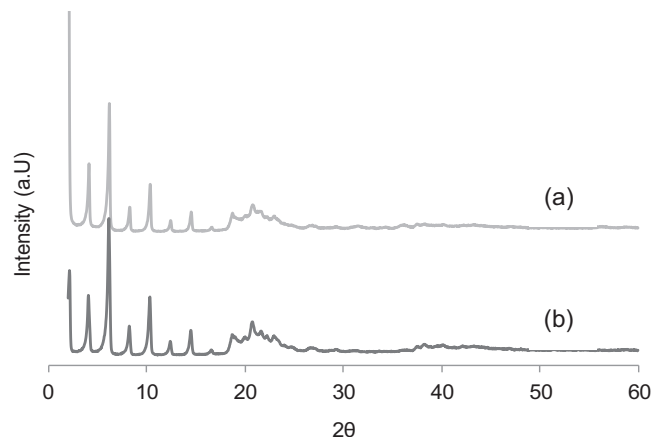


Fig. 18. XRD patterns of ZnGly after OA esterification at 100 °C (a) and 140 °C (b).

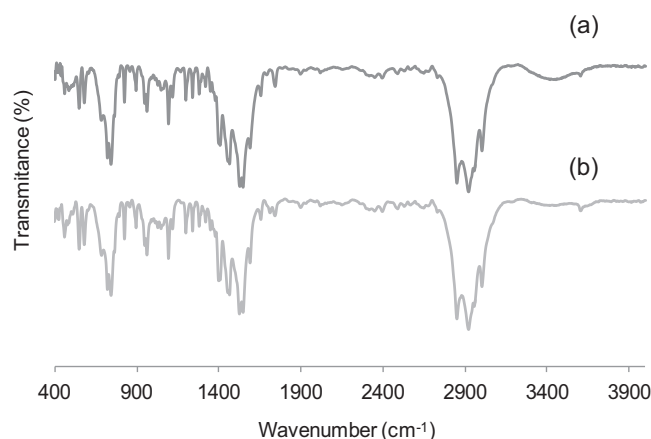
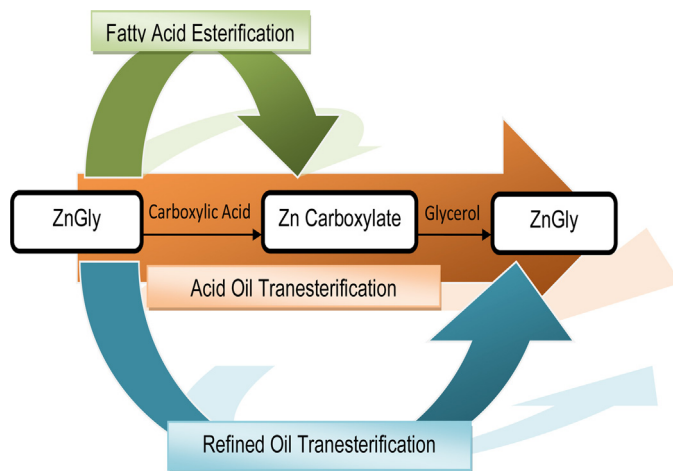


Fig. 19. DRIFT spectrum of ZnGly after OA esterification at 100 °C (a) and 140 °C (b).



Scheme 1. Transformation cycle of the catalyst in different reaction medium.

glycerolate reacts giving the corresponding Zn carboxylate salt. In all the cases, the final catalyst is an easily filterable powder.

## 4. Conclusions

Zinc glycerolate (prepared by a simple method) was able to convert soybean oil into fatty acid methyl esters with 66–76% yield and up to 95–97% triglyceride conversion in the 100–140 °C reaction temperature range.



This catalyst showed a long life and could be reused for five catalytic cycles without deactivation or selectivity loss.

ZnGly catalyst exhibited a good tolerance toward 0.5 wt.% water, without any important change in TG conversion, but with a 23% decrease in FAME yield.

On the other hand, in the presence of fatty acids ZnGly showed an almost complete TG conversion with an increase in FAME yield of 51% (93% FAME selectivity at 50 min reaction time). At 140 °C and in acid oil, ZnGly easily transformed into Zn carboxylate and partially re-generated in the presence of glycerol.

In summary, ZnGly was an active and environmentally-friendly catalyst for the production of biodiesel from soybean oil. Additionally, the Zn glycerolate-Zn carboxylate duo is an emergent catalytic system active with low-cost vegetable oils, and that can be easily separated from the reaction medium and reused without activation or cleaning treatments.

## Acknowledgements

The authors thank the Agencia Nacional de Promoción Científica y Tecnológica (National Agency of Scientific and Technological Promotion, Argentina) and the Consejo Nacional de Investigaciones Científicas y Técnicas (National Council for Scientific and Technological Research, CONICET) for the financial support.

## References

- [1] D. Reinoso, D. Damiani, G. Tonetto, *Applied Catalysis A* 449 (2012) 88–95.
- [2] D. Reinoso, M. Ferreira, G. Tonetto, *Journal of Molecular Catalysis A* 377 (2013) 29–41.
- [3] M. Kouzu, S. Yamanaka, J. Hidaka, M. Tsunomori, *Applied Catalysis* 355 (2009) 94–99.
- [4] M. Kouzu, M. Tsunomori, S. Yamanaka, J. Hidaka, *Advanced Powder Technology* 21 (2010) 488–494.
- [5] M. López Granados, A.C. Alba-Rubio, F. Vila, D. Martín Alonso, R. Mariscal, *Journal of Catalysis* 276 (2010) 229–236.
- [6] L. León-Reina, A. Cabeza, J. Rius, P. Maireles-Torres, A. Alba-Rubio, M. López Granados, *Journal of Catalysis* 300 (2013) 30–36.
- [7] M. Whitehouse, K. Rainsford, R. Taylor, B. Vernon-Roberts, *Agents and Actions* 3 (1990) 47–58.
- [8] D. Fairlie, M. Whitehouse, R. Taylor, *Agents and Actions* 36 (1992) 152–158.
- [9] R. Taylor, A. Brock, US Patent 4,544,761, 1985.
- [10] H. Dong, C. Feldmann, *Journal of Alloys and Compounds* 513 (2012) 125–129.
- [11] R. Cid, G. Pecchi, *Applied Catalysis* 14 (1987) 15–21.
- [12] K. Tanabe, M. Misono, Y. Ono, H. Hattori, *Studies in Surface Science and Catalysis* 51 (1989) 14.
- [13] X. Hou, Y. Qi, X. Qiao, G. Wang, Z. Qin, J. Wang, *Korean Journal of Chemical Engineering* 24 (2007) 311–313.
- [14] J. Das, D. Khushalani, *Journal of Physical Chemistry C* 114 (2010) 2544–2550.
- [15] T. Hambley, M. Snow, *Australian Journal of Chemistry* 36 (1983) 1249–1253.
- [16] F. Van Laar, D. De Vos, F. Pierard, A. Kirsch-De Mesmaeke, L. Fiermans, P. Jacobs, *Journal of Catalysis* 197 (2001) 139–150.
- [17] K. Westerterp, W. Van Swaaij, A. Beenackers, *Chemical Reactor Design and Operation*, John Wiley & Sons, New York, 1987.
- [18] H. Fogler, L. Scott, *Elements of Chemical Reaction Engineering*, 3rd ed., Prentice Hall, New Jersey, 1999.
- [19] J. Portha, F. Allain, V. Coupard, A. Dandeu, E. Girot, E. Schaer, L. Falk, *Chemical Engineering Journal* 207/208 (2012) 285–298.
- [20] C. Co, M. Tan, J. Diamante, L. Yan, R. Tan, L. Razon, *Catalysis Today* 174 (2011) 54–58.
- [21] V. Pugnet, S. Maury, V. Coupard, A. Dandeu, A. Quoineaud, J. Bonneau, D. Tichit, *Applied Catalysis A* 374 (2010) 71–78.
- [22] S. Yan, S. Mohan, C. DiMaggio, M. Kim, K.Y. Ng, S. Salley, *Fuel* 89 (2010) 2844–2852.
- [23] M. Di Serio, R. Tesser, L. Pengmei, E. Santacesaria, *Energy and Fuels* 22 (2008) 207–217.
- [24] Z. Yang, W. Xie, *Fuel Processing Technology* 88 (2007) 631–638.
- [25] K. Tanabe, K. Shimazu, H. Hattori, K. Shimazu, *Journal of Catalysis* 57 (1979) 35–40.
- [26] M. S. Dasari, E. Doskocil, P. Mankidy, M. Goff, *Applied Catalysis A* 257 (2004) 213–223.
- [27] J. Jitputti, B. Kitiyanan, P. Rangsunvigit, K. Bunyakit, L. Attanatho, P. Jenvanitpanjakul, *Chemical Engineering Journal* 116 (2006) 61–66.
- [28] H. Sun, Y. Ding, J. Duan, Q. Zhang, Z. Wang, H. Lou, X. Zheng, *Bioresource Technology* 101 (2010) 953–958.
- [29] R. Silva Rodrigo, J. Hernandez Enriquez, A. Castillo Mares, A. Melo Banda, R. Garcia Alamilla, M. Picquart, T. Lopez Goerne, *Catalysis Today* 107/108 (2005) 838–843.
- [30] R. Taylor, US Patent 20,060,173,073 A1, 2006.
- [31] X. Liu, X. Piao, Y. Wang, S. Zhu, *Energy and Fuels* 22 (2008) 1313–1317.
- [32] A. Zieba, A. Pacula, A. Drelinkiewicz, *Energy and Fuels* 24 (2010) 634–645.
- [33] B. Freedman, R. Butterfield, E. Pryde, *Journal of the American Oil Chemists Society* 63 (1986) 1375–1380.
- [34] D. Kumar, A. Ali, *Biomass and Bioenergy* 46 (2012) 459–468.
- [35] Y. Wang, H. Chou, B. Chen, D. Lee, *Bioresource Technology* (2013), <http://dx.doi.org/10.1016/j.biortech.2012.12.024>.
- [36] E. Xu, V. Rudolph, *Applied Catalysis B* 88 (2009) 42–49.